Novel Methylene Blue Sensitized Photopolymers for Holographic Recording: a Comparison

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Polymer matrices like PVC and a blend of PVA/PAA is introduced as new holographic media that cause red sensitivity with methylene blue. Unlike methylene blue sensitized polymers like PVA, PMMA, gelatin etc, the change of state occurring for methylene blue on laser irradiation on PVC matrix was found to be permanent. No recovery of dye on the irradiated spot was observed on storage. The outstanding properties of this material are its excellent optical clarity, insensitive to humidity, economical, ease of fabrication, absence of dark room storage etc. The recovery of dye in conventional MBPVA matrix can be delayed by blending PVA with PAA. Optimization of the ratio of PVA/PAA, the sensitizer concentration, pH, energy, diffraction efficiency measurements etc are done. pH is found to have a great influence on the recovery of the dye in this matrix. The effect of monomers in improving the diffraction efficiency on these dye doped polymer system is also evaluated. A comparative study is done on these polymer matrices and holographic gratings were recorded on these films from a He- Ne laser operating at 632.8 nm.
Key Word: Methylene blue, poly (vinyl chloride), poly acrylic acid, diffraction efficiency, gratings.

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1. INTRODUCTION`

Holographic data storage has been considered as one of the new generation information storage technologies because of its potential for high storage capacity (10^{12} bits/cm^2) and fast read out speed (10^{11}bits/sec) [1-3]. Availability of suitable recording material is the key to the success of holographic memories. So far, the most popular material for this application is photopolymers. They are of interest because of their large refractive index contrast; high photosensitivity, low cost, environmental stability and they can be easily synthesized to have different compositions [4-5]. Extensive studies have been done on methylene blue sensitized polymers like PVA, gelatin, PMMA, and the results were found to be very promising. But the main draw back of these systems was that the information stored on these films was not stable for a long time and chemical treatment was necessary for fixing the data. Moreover they need dark room storage and are highly sensitive to humidity. We have introduced few dye sensitized photopolymers which have the advantage of good shelf life, low noise, good photosensitivity, low cost, absence of dark room storage, insensitive to humidity with good environmental stability etc. This article deals with the preparation and characterization of two methylene blue sensitized polymer matrices namely methylene blue sensitized poly (vinyl chloride) and methylene blue sensitized polymer blend of poly (vinyl alcohol) and poly acrylic acid fabricated in our laboratory.

Poly (vinyl chloride) (PVC) has been chosen as one of the polymer matrix due to its unique properties like excellent optical properties, colourability, dimensional and environmental stability, ease of fabrication, low cost, flexible or rigid, non-toxic, stability against U.V light, transparency in the visible spectral region and insensitive to humidity. It can also be fabricated to any desired thickness. The suitability of using PVC for hologram recording is already reported [6,7]. Methylene blue in poly (vinyl chloride) is a good medium for optical recording; we were able to enhance the sensitivity of this film by converting the dye to a more stable complexed state with the use of copper (II) acetate as the complexing agent.

2. EXPERIMENTAL

Copper acetate sensitized methylene blue doped poly (vinyl chloride) (CMBPVC)

The preparation of complexed methylene blue sensitized poly (vinyl chloride) (CMBPVC) films involves the deposition of the sensitized PVC from solution on a suitable substrate and allowing the solvent to evaporate slowly. There are different techniques employed for coating, but in the present work we have adopted gravity settling method. The coating solution consists of a polymer (PVC), a sensitizer (MB), a complexing agent (copper acetate), a solvent for the polymer (cyclohexanone) and a solvent for the dye (glacial acetic acid).

All the samples were prepared under normal laboratory conditions as follows:

1. Poly (vinyl chloride) was dissolved in cyclohexanone at room temperature to yield a solution having 13.5 weight % of PVC.
2. Crystals of methylene blue and copper acetate were dissolved in the ratio 2:1 in glacial acetic acid to obtain the desired dye concentration.

A homogeneous solution of the dye and PVC was obtained by mixing a fixed volume complexed methylene blue with the PVC solution.

Preparation of methylene blue sensitized poly (vinyl alcohol)/poly (acrylic acid) blend [MBPVA/PAA]

A 10% solution of poly (acrylic acid) (PAA) was prepared by refluxing acrylic acid (10 ml), water (90g), potassium persulphate (0.2g) at 90 ^{0}C in a three necked flask fitted with an additional funnel, reflux condenser, thermometer and a stirrer. The heating is done for 4 h. The 10%PAA solution thus obtained was mixed with 10%PVA in the ratio 3:7 in methanol (20 ml). This mixture was then sensitized with methylene blue solution. The films were prepared as explained in CMBPVC. The studies were carried for an optimum dye concentration and pH [table 1]

Laser Exposure

To study the effect of laser exposure on these films a Coherent Melles Griot He-Ne laser with emission at 632.8 nm was used. The laser beam was expanded and filtered using a spatial filter arrangement set up in the laboratory [8]. The samples were placed in the expanded beam. The transmittance value of the undoped sample was taken as T^0 and that obtained for the dye sensitized film was taken as T and their ratio T/T^0 was found out for standardization. The effect of He-Ne laser irradiation on the absorption spectra of the methylene blue sensitized films was studied using a Hitachi 30 UV-VIS-NIR spectrophotometer. The experimental set up used for diffraction efficiency measurements are shown in fig 1&2.

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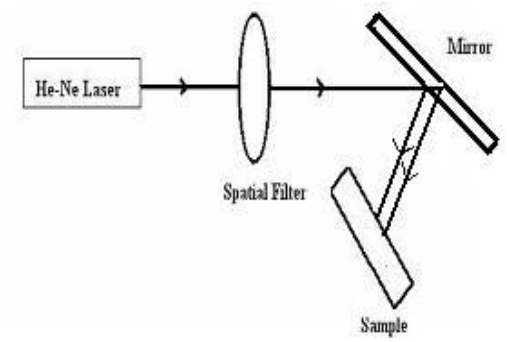

Fig 1. Experimental set up used for recording interference pattern

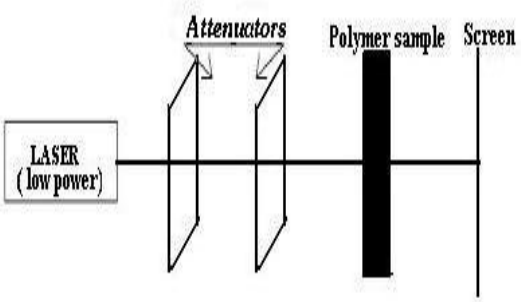

Fig 2. Experimental set up used for measuring diffraction efficiency

3. RESULTS AND DISCUSSION

Optical absorption studies

The typical absorption spectra of the unexposed exposed and after 48 h of laser irradiation of samples of MBPVA/PAA blend, and CMBPVC, are shown in figure 3&4, respectively. The exposure time was kept as 5 min for these samples for a power density of 5mW/cm^2. On laser irradiation the dye gets converted to the leuco form that is colourless. In the case of MBPVA/PAA blend the conversion of leuco form to the stable thionine state[8] was found to be rather slow even though a small shift (664-654 nm) was observed after irradiation. The recovery to the thionine state was almost complete in three weeks. It has been found that as the poly (vinyl alcohol) content in the blend increases, the rate of reconversion of the dye increases. In the absence of PAA i.e. in MBPVA films the recovery of dye was almost complete in 36h. So it

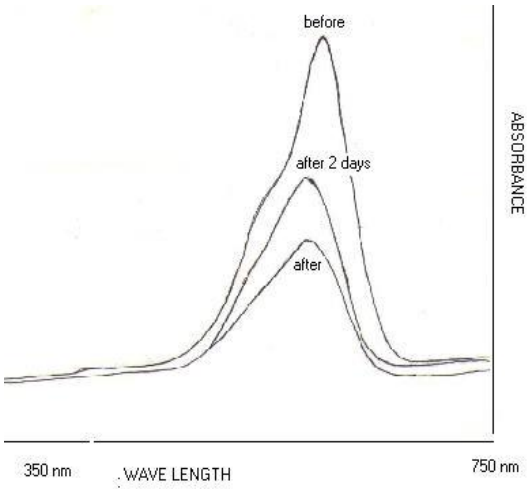

Fig 3. Optical absorption spectra of MBPVA/PAA blend

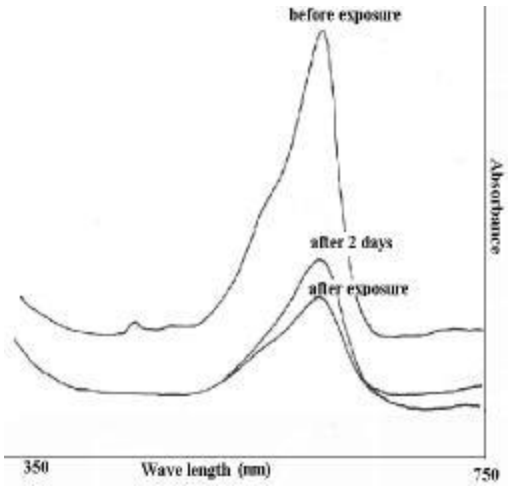

Fig 4. Optical absorption spectra of CMBPVC

is evident that poly (acrylic acid) content in the blend plays a very important role on the recovery of the dye in this matrix. From the fig 4 it is clear that no shift in absorption spectrum was found on irradiation in CMBPVC films i.e. the leuco form of methylene blue is very stable in PVC matrix and no recovery of dye was observed for several months. From this observation it is clear that the polymer matrix plays a unique role in the different dye behavior.

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Effect of Storage

Long storage life was a perquisite for the materials to be used for optical recording. The change in absorption at the irradiated spot was monitored as a function of time and is plotted in figure 5. A small decrease in the change in absorbance at the irradiated spot was observed initially for MB in PVA/PAA film. Where as in the case of CMBPVC films, there was not much absorbance change with time, proving itself to be useful for permanent recording.

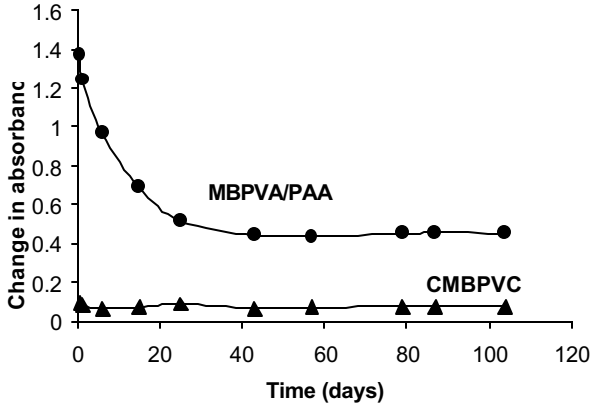

Fig 5. A plot of change in absorbance with time for MBPVA/PAA and CMBPVC films

Interferometric Studies

Gratings of different spatial frequencies were recorded on MBPVA/PAA blend film and CMBPVC film and diffraction efficiencies were measured in all the cases. It has been found that maximum diffraction efficiency was observed for a fixed exposure at an interfering angle of 40^0 for MBPVA/PAA blend and CMBPVC films. So a detailed study was done at this angle for different exposures. Maximum diffraction efficiency of about 11% and 4.8% has been achieved for MBPVA/PAA blend and CMBPVC respectively at a fixed spatial frequency of 588 lines/mm. Even though the film property of the polymer blend is not superior to MBPVA films, a maximum diffraction efficiency of 11% was achieved for this polymer blend. These diffraction efficiencies were achieved on all the samples without any fixing or development. Comparison of variation of diffraction efficiency of MBPVA/PAA blend film, CMBPVC, with energy is shown in figure 6.

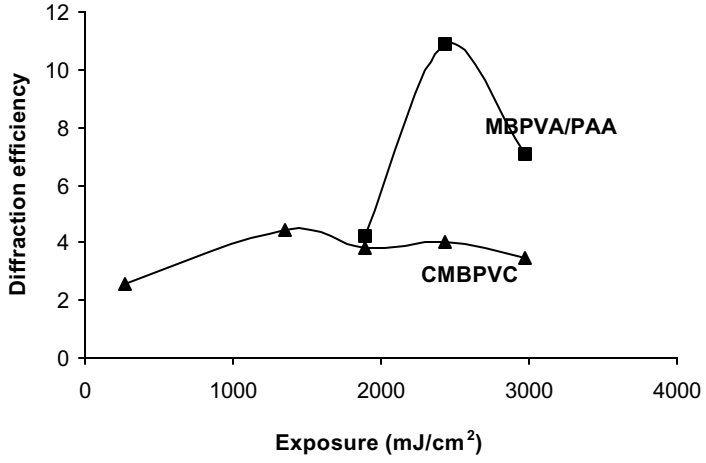

Fig 6. Variation of diffraction efficiency with exposure at an angle 40^0

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The variation of diffraction efficiency may be due to the different modes of behaviour of methylene blue in different polymer matrices. In the exposed area, the dye was partially or totally bleached, however if the plate was left in a light tight container, after few hours the dye returned to its original colour. This was true in the case of MBPVA/PAA blend. However, even if the films recovered its original colour, on illuminating the irradiated area with a red beam the diffracted orders could be seen. This implies that the dye passed through a transition state to the leuco form or the excited state, and then decayed to the ground state. However, the polymerization of the exposed area remained, even though the dye recovered when in the dark. The time taken for the recovery of the dye is different in different polymer matrices. This implies that polymerization in different matrices are different. In the case of CMBPVC, the chance of further polymerization is less, since there is no residual monomer in the matrix. It may be the reason why the diffracted pattern recorded on CMBPVC films are not stable, even though the irradiated part will not regain colour on standing. This matrix is therefore very much suitable for direct imaging, but not good for holographic applications. The photograph of the first and second order diffracted pattern obtained on these materials is shown in figure 7&8.

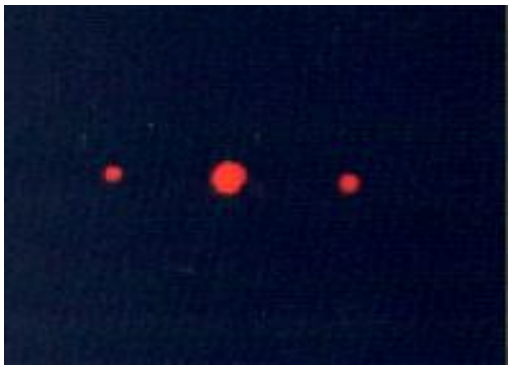

Fig 7. Photograph of first order diffracted pattern obtained on CMBPVC films

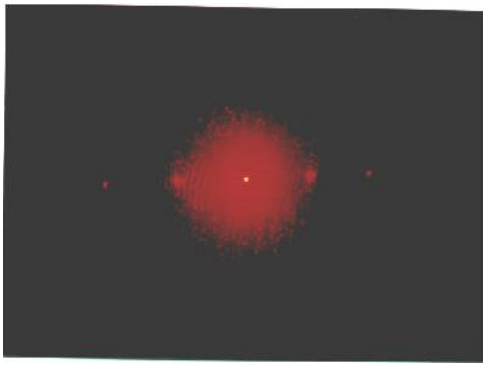

Fig 8. Photograph of first order diffracted pattern obtained on MBPVA /PAA

Self-Enhancement

An enhancement effect, reinforcement, has been demonstrated in MBPVA/PAA films. The observed self-enhancement for methylene blue sensitized films is a remarkable change in the diffracted beam. After the recording was stopped, the diffraction efficiency increased. In the case of blend, the diffraction efficiency of ~11% increased to only ~14% over 15 days (fig 9). The rate of self-enhancement was highest during the first day after the recording, appearing to be near saturation after ~15 days. The humidity was not changed during the storage of the MBPVA/PAA gratings and the grating was stored the entire time in the same room conditions that they were recorded. After 20 days the diffraction grating recorded on these samples almost vanished. This shows that a proper fixing method is necessary to fix the leuco dye in the polymer matrix.

This self-enhancement may be due to the following reasons:

a) Dark reaction b) Diffusion c) Polymerization

Polymerization may be responsible for the self-enhancement of the holographic grating in MBPVA/PAA films. The mechanism is yet to be evaluated. This dark reaction was considered earlier to be a disadvantage. Now we know that the dark reaction after recording does not distort the diffraction efficiency of the grating but increases it. This effect offers the possibility of using this material in real time measurements for longer periods. The use of self-enhancement is of great interest in hologram recording also by facilitating shorter exposures and thus vibration free exposures. In the case of CMBPVC films, no self-enhancement was observed. It can be due to the lack of residual polymerization on CMBPVC films on laser irradiation. The grating was stored for the entire time in the same room conditions that they were recorded**.** It is well known that two processes can be initiated by exposure to red light: polymerization and dye fixing. Unlike in other polymer matrices like PVA, PMMA, gelatin, the change in residual polymerization is less in PVC since the monomer is a gas and its concentration is very low in the polymer and hence the chance of polymerization of the residual monomer in the illuminated area is negligible. So a change in refractive index is not expected. No change in absorption at the unexposed part was observed; hence the migration of dye molecules to those areas on illumination can be ruled out.

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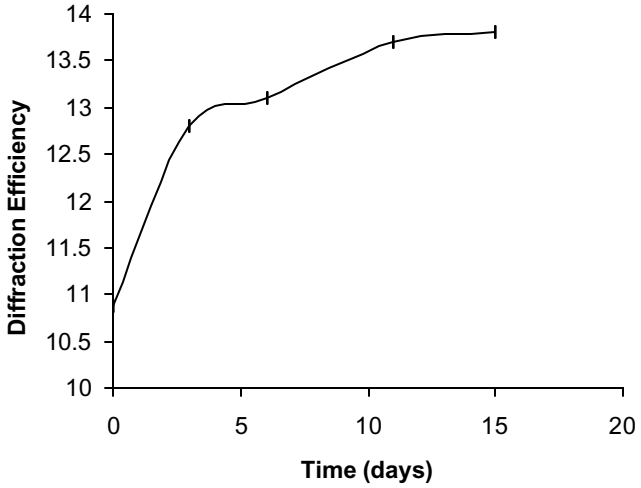

Fig.9. Change in diffraction efficiency after exposure for MBPVA/PAA films

Complexed dye molecules that are converted into the leuco form in the polymer matrix will become fixed in their location, resulting in a concentration gradient of the free dye molecules in the material. Thus the recorded images were permanent. Materials that operate in a principle similar to that described here have also recently been developed for holographic memories [9]. An outstanding property of this material is that it is least affected by humidity, since PVC has no affinity towards moisture. Moreover it does not need any dark room storage as in the case of other methylene blue sensitized conventional polymer systems. Whereas in the case of MBPVA/PAA blend, recovery of dye was observed on storage.

Direct Imaging

An attempt was made to do direct imaging on the optimized CMBPVC and MBPVA/PAA films. The medium consists of an inert polymer host on which the complexed methylene blue molecules are uniformly suspended. The writing wavelength of this material is determined by the photosensitizer (MB), which in this case has an absorption peak close to

Fig 10.A photograph of few alphabets recorded on MBPVA/PAA film

Fig 11. A photograph of small words recorded on CMBPVC film

red 632.8nm line of He-Ne laser. Hence an expanded beam of 10 mW He-Ne laser was passed through a transparent sheet on which letters were written and the transmitted beam was allowed to fall on the CMBPVC film placed on a film holder. The beam was allowed to fall on the material for 5 min. After the imaging it could be observed that the letters were very legible with good contrast and no scattering centers (figure10, 11) were found in the exposed region. The same results were observed in the case of MBPVA/PAA films also. It could be observed that the fabricated films were of good optical quality. We could also ascertain that the films could record letters of small size. This could give a

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qualitative idea about the resolution capacity of the material. The mechanism of recording in this material is explained in[7].

The role of copper acetate and glacial acetic acid in fixing this dye to its leuco form in CMBPVC can be ruled out because in a similar experiment done on complexed methylene blue sensitized poly (vinyl alcohol) showed that the dye recovered to its original color after 24 hours. Hence the role of PVC in this dye behavior is prominent. No degradation product was formed at the irradiated area. This was confirmed by dissolving the irradiated portion in cyclohexanone. The exact role of PVC in this dye behavior is not fully known.

In the case of MBPVA/PAA, the polyacrylic acid content in the blend, greatly influence the dye behavior. As the PAA content in the blend increases, the recovery of dye from leuco form to original form was also delayed. But we could not increase PAA content in the blend beyond a certain limit, because it adversely influences the film property. The conversion of methylene blue to its leuco form could be made fixed by changing the polymer matrix. We have already explained that complexed methylene blue in poly (vinyl chloride) can be used as a permanent recording material for direct imaging. In this case the conversion of leuco methylene blue back to its original form was found to be a very slow process (even after 6 months the recovery was not observed) and hence this material proves to be useful for optical recording with out any chemical treatment. But the diffraction efficiency was very low. Studies are going on to improve diffraction efficiency by incorporating suitable monomers into this system. MBPVA/PAA blend gives approximately 11% diffraction efficiency and shows only very slow recovery.

A comparative study on the methylene blue sensitized polymers CMBPVC and MBPVA/PAA is summarized in Table 1

Table 1. Comparison of the optical parameters of CMBPVC and MBPVA/PAA films

Properties	**CMBPVC**	**MBPVA/PAA**
Solvent	Cyclohexanone	methanol
Dye	MB	MB
Complexing agent	Copper acetate	-
Wave length range of dye	665nm	665nm
Shift in absorption spectra	No shift	Small Shift
Optimum dye conc.	1.28×10^{-3} mol/l.	1.46×10^{-4} mol/l
Optimum pH	4.5	3.8
Recovery of dye	No	Yes, very slow
Threshold energy	300 mJ	200mJ
Saturation energy	400mJ	1800mJ
Max diffraction efficiency	4.8%	11%
Self enhancement	No	Yes

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4.CONCLUSIONS

MBPVA/PAA and CMBPVC are introduced as high sensitive media for optical recording. CMBPVC is insensitive to humidity, unlike other methylene blue sensitized polymer films. Characterization of CMBPVC films revealed that they have excellent shelf life, storage life and the change of state occurring for methylene blue on laser irradiation is permanent in this matrix and can be used as a permanent recording material. In the case of MBPVA/PAA, the recovery of dye on laser irradiation can be controlled by changing the pH and amount of PAA in the blend. It is very interesting to note that the same dye shows different behavior under same exposure conditions on different polymers. Diffraction efficiency of about 11% and 4.8% was obtained on MBPVA/PAA and CMBPVC respectively with out any fixing process. The major attractions of these materials are its excellent optical clarity, environmental stability, ease of recording, low cost etc. Self-enhancement in diffraction efficiency was observed on MBPVA/PAA films.

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